

Spin freezing and slow magnetization dynamics in geometrically frustrated magnetic molecules with exchange disorder

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We show that intramolecular exchange disorder recently found in the geometrically frustrated magnetic molecules $\{\text{Mo}_{72}\text{Fe}_{30}\}$ and $\{\text{Mo}_{72}\text{Cr}_{30}\}$ leads in a classical Heisenberg model description to spin freezing and slow magnetization dynamics reminiscent of spin glass behavior. Our low temperature and low magnetic field NMR measurements on these molecules are explained as a cross-over of the proton line width from paramagnetic behavior to a frozen spin configuration at about 400 mK.

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Geometrical frustration is the source for a variety of fascinating phenomena that have been observed in magnetic materials [1]. It arises in lattices that are composed of magnetically frustrated building blocks, such as anti-ferromagnetically coupled spins on triangles or tetrahedra. Experimental studies on two-dimensional Kagome lattice compounds (composed of corner-sharing triangles) and three-dimensional pyrochlores (composed of corner-sharing tetrahedra) show spin freezing at sufficiently low temperatures [2]. The origin of this spin freezing has long been puzzling. Theoretical studies have shown that the observed spin glass behavior cannot be explained by geometrical frustration alone [3–5]. Instead, it has been found that weak exchange randomness in the classical Heisenberg antiferromagnet on the pyrochlore lattice is responsible for a spin glass transition at a temperature set by the disorder strength [3]. This result is consistent with the accepted view that spin glass behavior has two prerequisites, frustration and randomness [12]. The combination of both requirements lead to highly degenerate free-energy landscapes with a distribution of barriers between different metastable states, resulting in broken ergodicity below a characteristic spin freezing temperature T_f .

Here we present the first experimental and theoretical evidence for spin freezing and slow magnetization dynamics in a class of *zero-dimensional* strongly frustrated systems, specifically, the pair of Keplerate magnetic molecules abbreviated as $\{\text{Mo}_{72}\text{Fe}_{30}\}$ and $\{\text{Mo}_{72}\text{Cr}_{30}\}$ [6, 7]. We attribute this behavior to the occurrence of intra-molecular exchange disorder of the 30 interacting magnetic ions that has recently been found in both molecules [9].

In the magnetic molecules $\{\text{Mo}_{72}\text{Fe}_{30}\}$ and $\{\text{Mo}_{72}\text{Cr}_{30}\}$ the magnetic ions Fe^{III} (spin $s = 5/2$) and Cr^{III} (spin $s = 3/2$) occupy the 30 sites of an icosidodecahedron, a closed spherical structure consisting of 20 corner-sharing triangles arranged around 12 pentagons. Consequently, this structure serves as a zero-dimensional analogue of the planar Kagome lattice that is composed of corner-sharing triangles arranged around hexagons. Most important, these compounds are realized as crystals of identical molecular units, where inter-molecular magnetic interactions are negligible as compared to intra-molecular magnetic interactions. Measurements of the magnetic properties therefore reflect those of the common, individual molecular unit. In previous work it has been shown that the magnetic properties of both molecules can accurately be described by an isotropic nearest-neighbor *classical* Heisenberg model of interacting spins [8, 9, 13]. For $T > 5$ K one can use a single antiferromagnetic exchange constant $J_c = Js(s + 1)$ (in units of Boltzmann’s constant k_B) with values [13] of 13.74 K and 32.63 K for $\{\text{Mo}_{72}\text{Fe}_{30}\}$ and $\{\text{Mo}_{72}\text{Cr}_{30}\}$, respectively. However, recent low temperature and low magnetic field measurements ($T < 5$ K) of the magnetic susceptibility of $\{\text{Mo}_{72}\text{Fe}_{30}\}$ and $\{\text{Mo}_{72}\text{Cr}_{30}\}$ have revealed the existence of a modified interaction scenario where the 60 nearest-neighbor interactions are not identical. Instead, the exchange interactions are disordered, characterized by a two-parameter probability distribution whose mean value is J_c [9].

We find manifestations of spin freezing and slow magnetization dynamics, due to the exchange disorder in both molecules, in three distinct calculated quantities: 1)

the thermal averaged *local* moments; 2) the time decay of the thermoremanent dc magnetization (TRM); and 3) field-cooled (FC) and zero-field cooled (ZFC) susceptibility. Our experimental evidence for spin freezing is provided below. Using the probability distribution parameters as given in [9] the exchange couplings for the 60 nearest-neighbor pairs are chosen to be uniformly distributed in the range $[(1 - \rho)J_c, (1 + \rho)J_c]$, where the half-width of the distribution is chosen as $\rho = 0.4$, and the mean of the distribution, J_c , is listed earlier. By comparison, for a single- J scenario (i.e., without exchange disorder) we find that spin freezing and slow magnetization dynamics are absent.

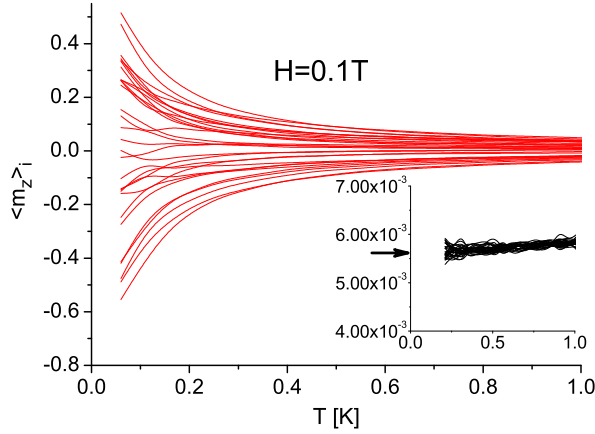


FIG. 1: Results of classical Monte Carlo simulations for a model system of $\{\text{Mo}_{72}\text{Fe}_{30}\}$ in a magnetic field $\vec{H} = H\vec{e}_z$, where $H = 0.1\text{ T}$. Due to exchange disorder the local spin variables $\langle m_z \rangle_i$ (see [13]) of the 30 iron sites display spin freezing. In the absence of exchange disorder (inset) the simulation results approach the exact $T = 0\text{ K}$ theoretical result of [10], $\langle m_z \rangle_i = H/H_s = 5.65 \cdot 10^{-3}$, independent of i (indicated by the black arrow).

In Fig. 1 we show the thermal average of the classical spin vectors $\langle m_z \rangle_i$ due to a magnetic field $\vec{H} = H\vec{e}_z$ for $H = 0.1\text{ T}$ as a function of temperature for each of the 30 iron sites for the exchange disorder model of $\{\text{Mo}_{72}\text{Fe}_{30}\}$ as obtained by classical Monte Carlo simulations [13]. Already for temperatures larger than $T \approx 1\text{ K}$ the $\langle m_z \rangle_i$ are nearly independent of i and proportional to H , and the results are in agreement with those for the single- J model for all T (see inset). However, below $T \approx 1\text{ K}$ the values of $\langle m_z \rangle_i$ span almost the entire range from -1 to $+1$. Thus, in the exchange disordered case, there exists a preferred direction parallel or anti-parallel to the direction of the external field that persists during the averaging process, i.e., the spins are *frozen* [11].

In order to verify this freezing behavior experimentally we have performed proton NMR measurements on

both $\{\text{Mo}_{72}\text{Fe}_{30}\}$ and $\{\text{Mo}_{72}\text{Cr}_{30}\}$. NMR provides a local probe sensitive to the local spin components of the magnetic moments via the nuclear-electron dipolar interaction. The second moment of the proton NMR line due to the interaction with the Fe (Cr) moments is given by $\langle \Delta\nu^2 \rangle = \sum_i \langle (\nu_R^i - \nu_0)^2 \rangle = \sum_i \gamma^2 \left[\sum_j \langle m_z \rangle_j A(\theta_{ij})/r_{ij}^3 \right]^2$ where $A(\theta_{ij})/r_{ij}^3$ are the dipolar coupling constants between nucleus i and electron moment j , ν_R^i is the resonance frequency of nucleus i and ν_0 is the Larmor frequency of the proton with gyromagnetic ratio γ . The spin freezing shown in Fig. 1 generates an increase of the local spin moment $\langle m_z \rangle_i$ as compared to the paramagnetic case and this gives rise to a dramatic increase of the proton NMR second moment, i.e. the proton line width. Broadening would be absent for the single- J scenario where the local spin components of the magnetic moments are very small at each lattice site. In Fig. 2 we show the proton line width data for $\{\text{Mo}_{72}\text{Fe}_{30}\}$ at a low external magnetic field (0.16 T). The corresponding proton NMR spectra for several temperatures are shown in the upper inset. A dramatic broadening of the line width is clearly observed starting at about 400 mK. The line width data for $\{\text{Mo}_{72}\text{Cr}_{30}\}$ at a higher magnetic field (1 T) are shown in the lower inset. Also for this system there is significant broadening of the line width at low temperatures however it is more gradual than for $\{\text{Mo}_{72}\text{Fe}_{30}\}$. This is due to both the higher field value and the larger exchange interaction in the case of $\{\text{Mo}_{72}\text{Cr}_{30}\}$. The solid horizontal line in each graph, marking the value of the T independent nuclear

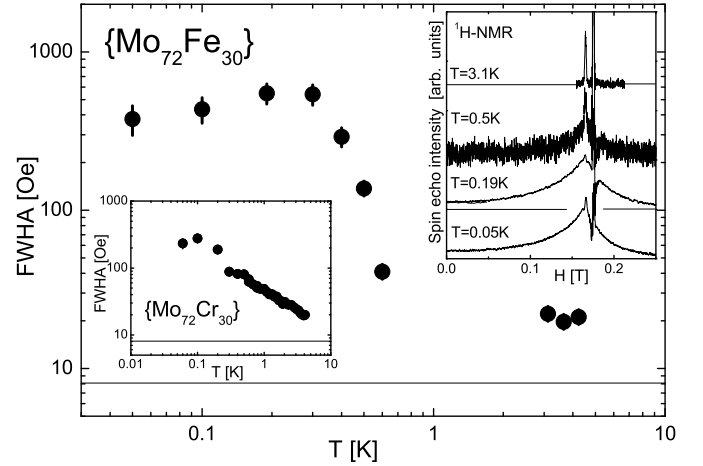


FIG. 2: Proton NMR line width in $\{\text{Mo}_{72}\text{Fe}_{30}\}$ for $H = 0.16\text{ T}$. The horizontal line gives the T independent nuclear dipolar width. The lower inset shows the corresponding results for $\{\text{Mo}_{72}\text{Cr}_{30}\}$ for $H = 1\text{ T}$. The upper inset shows some proton NMR spectra measured at $f = 7.03\text{ MHz}$ at different temperatures (the narrow shifted line is the ^{19}F NMR marker).

dipolar width, gives an idea of what the width would be without the contribution of local moments at the Fe (Cr) sites. Thus in both $\{\text{Mo}_{72}\text{Fe}_{30}\}$ and $\{\text{Mo}_{72}\text{Cr}_{30}\}$ one observes experimentally spin freezing in excellent agreement with the above theoretical scenario of spin freezing due to exchange disorder. We note that a frozen spin state in NMR is defined as the state in which the correlation time of the fluctuations of the local moment $m_{z,j}$ becomes of the order of the static nuclear-electron dipolar interaction estimated for $\{\text{Mo}_{72}\text{Fe}_{30}\}$ to be of the order of 500 Oe (or 2 MHz) from the limiting low temperature line width in Fig. 2. In $\{\text{Mo}_{72}\text{Cr}_{30}\}$ the limiting line width is smaller than that of $\{\text{Mo}_{72}\text{Fe}_{30}\}$ in spite of the higher applied magnetic field, reflecting the fact that the susceptibility, and thus also the static nuclear-electronic dipolar field, is smaller in $\{\text{Mo}_{72}\text{Cr}_{30}\}$ by more than a factor of two [9].

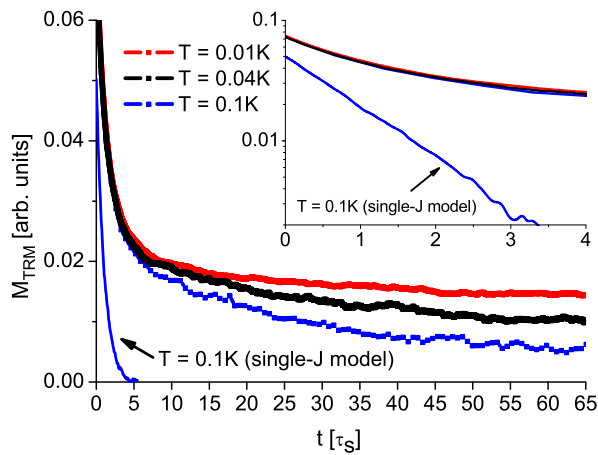


FIG. 3: Simulated TRM time-decays of the FC magnetization ($H_{FC} = 0.1$ T) of a model system of $\{\text{Mo}_{72}\text{Fe}_{30}\}$ with and without exchange disorder for temperatures given in the legends. The time variable is scaled in units of the lifetime, τ_s , of the single- J model, as explained in the text.

Other indications of spin freezing include the slow relaxation of the TRM in the freezing regime and a characteristic difference between FC and ZFC susceptibilities. An effective method for investigating these properties is to use the numerical solution of the stochastic Landau-Lifshitz equation which simulates the time evolution of the spin system coupled to the heat bath [14]. Fluctuating fields are used to account for the effects of the interaction of the spin system with the heat bath. Those environmental degrees of freedom are also responsible for the damped precession of the magnetization parameterized by a phenomenological damping factor λ . The value of λ is unknown for the systems under study, so we have chosen $\lambda = 0.1$ which is a common value used in the study of magnetization relaxation in nanoparticles [15].

Fig. 3 shows our simulation results for TRM time-decays of the FC magnetization ($H_{FC} = 0.1$ T) of a model system of $\{\text{Mo}_{72}\text{Fe}_{30}\}$ with and without exchange disorder. We have used the following simplified protocol for such a simulation: The system is cooled in a field $H_{FC} = 0.1$ T to a measuring temperature T_m in the freezing regime. This is done at a rate of 10^7 time steps per Kelvin. At T_m the field is suddenly reduced to zero. The subsequent relaxation of the magnetization is then sampled. To achieve satisfactory statistics we have performed averages over 100 identical model systems. We have performed simulations at $T_m = 0.1$ K for both the exchange disordered and the single- J model for a direct comparison. In the inset of Fig. 3 we show a semi-log plot of the time decays in the short-time regime. One clearly sees that the single- J model of $\{\text{Mo}_{72}\text{Fe}_{30}\}$ (the lowest curve) shows a fast exponential decay as expected for a magnetic system with a flat free-energy landscape. For further comparison we have determined the corresponding lifetime τ_s , and use that as our time unit. The upper three curves correspond to the exchange disordered model for $T_m = 0.1, 0.04$ and 0.01 K. Here, we find non-exponential decay with identical characteristics independent of temperature. In the main panel of Fig. 3 we show the long-time behavior of the TRM decay. For the exchange disordered model the rapid relaxation within the first $5\tau_s$ is followed by a very slow decay. A first analysis of the functional form of the time decay is approximately consistent with a $\log(t)$ dependence for $t > 8\tau_s$. However, further detailed simulations are needed to establish an accurate functional form.

In Fig. 4 we show our results for the FC and ZFC susceptibility for a model of $\{\text{Mo}_{72}\text{Fe}_{30}\}$ with and without (inset) exchange disorder. In our simulations the system is cooled down from $T = 5.0$ K in zero field at a rate $2 \cdot 10^7$ time steps per Kelvin. At $T = 0.1$ K an external field of $H = 1.0$ T is switched on and the system is heated up to $T = 5.0$ K at the same rate while the magnetization is sampled. The system is again cooled down yielding the FC curve. The behavior shown in Fig. 4 is consistent with that for spin glass systems, namely a characteristic difference between the FC and ZFC curves below a certain branching temperature which is $T \approx 1$ K in our case. We also find that the branching of the FC and ZFC curves is field dependent: With increasing field the branching temperature is reduced. As shown in the inset, for the single- J case there is no significant difference between the FC and ZFC susceptibilities.

Another interesting question regarding the effect of exchange disorder is whether or not there exists a disordered but unique groundstate. For spin glasses one expects a highly degenerate free-energy landscape with a distribution of barriers between different metastable states. Using spin dynamics with Landau-Lifshitz damping we have performed 1000 simulations at $T = 0$ and $H = 0$ starting from different random initial spin configurations.

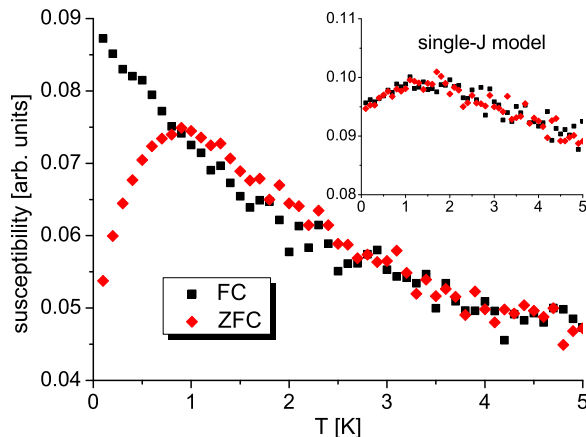


FIG. 4: Simulation of FC and ZFC susceptibility for a model of $\{\text{Mo}_{72}\text{Fe}_{30}\}$ with and without (inset) exchange disorder. The parameters of the simulation are given in the text.

urations and subsequent relaxation. The damping term generally drives the spin configuration towards a minimum of the total energy. We have performed such simulations for a single- J scenario as well as for an exchange disordered one. In the first case there exists a unique classical groundstate with a minimal energy value as given in [10]. However, in the disordered case we find a distribution of spin configurations of low energies, but cannot identify a unique ground state. These configurations have energies that are equivalent within a few percent of each other, supporting the picture that in the exchange disordered case the free-energy landscape consists of a distribution of barriers between different metastable states.

In summary, we have shown that the pair of magnetic molecules $\{\text{Mo}_{72}\text{Fe}_{30}\}$ and $\{\text{Mo}_{72}\text{Cr}_{30}\}$ display spin freezing and slow low temperature dynamics reminiscent of spin glass behavior due to disorder of the intramolecular exchange interaction. Our theoretical calculations predict a low-temperature, low-field variation of the local magnetic moments that we have observed by proton NMR measurements. Furthermore, our calculations strongly suggest that the free-energy landscape for the spin configurations in a single molecule consists of a distribution of barriers between different metastable states. As a consequence we predict that measurements of the TRM decay-times and the FC and ZFC susceptibility would show spin glass behavior. It is striking that spin glass type behavior occurs in such molecules. This gives us the unique opportunity to study glassy spin dynamics in *zero-dimensional* systems not just theoretically, but also experimentally. We expect that further comprehensive theoretical and experimental investigations on these systems will contribute towards a deeper understanding

of spin glass behavior in general.

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